



# PATENT SPECIFICATION

NO DRAWINGS

1020,201

Date of Application and filing Complete Specification: March 18, 1963.

No. 10633/63.

Application made in Germany (No. F36301 IVc/39b) on March 17, 1962.

Complete Specification Published: Feb. 16, 1966.

© Crown Copyright 1966.

Index at acceptance:—C3 R(32A, 32C6, 32C9, 32C10, 32C11, 32D1, 32D3, 32D6, 32E1, 32E3, 32E8, 32E9, 32F, 32G1, 32G2); C3 C1E2

Int. Cl.:—C 08 g // C 08 j

The inventors of this invention in the sense of being the devisers thereof within the meaning of Section 16 of the Patents Act 1949 are:—**HARALD OERTEL**, Leverkusen, Lindenstrasse 12, Germany; **HEINRICH RINKE**, Leverkusen, Saarlauterner Strasse 15, Germany; **WILHELM THOMA**, Köln-Flittard, Roggendorfstrasse 49, Germany, all German Citizens.

## COMPLETE SPECIFICATION

### Stabilisation of Synthetic Plastics Containing Urethane Groups against Discolouration and Oxidation

We, **FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT** of Leverkusen - Bayerwerk, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This application relates to synthetic plastics containing urethane groups and stabilised against discolouration and oxidation.

Synthetic plastics containing urethane groups have found uses as materials, foils, coatings, lacquers, foam materials and fibres, because of their good elastic properties, tensile strength and resistance to further tearing, to abrasion and to hydrolysis. These synthetic plastics containing urethane groups may be produced, in a variety of processes, by the isocyanate polyaddition process from polyhydroxy compounds of relatively high molecular weight and excess polyisocyanates, if desired in the presence of chain extenders containing active hydrogen atoms, such as water, glycols, polyamines, hydrazine and hydrazides.

Polyurethanes may also be obtained by other processes, for example by reacting chlorocarbonic acid ester of polyhydroxy compounds of relatively high molecular weight with, for example, diamines. The products obtained by these latter processes have the same structure and properties as those obtained by the isocyanate polyaddition process.

For many uses, however, it has so far been a disadvantage that many polyurethanes are not sufficiently stable to light (sunlight or ultra-violet), especially in the presence of

oxygen (air). This is particularly true of foam materials, foils, coatings and fibres.

It is known to produce products having relatively good light stability by using aliphatic diisocyanates, such as hexamethylene diisocyanate, in the formation of the synthetic plastics. Moreover, synthetic plastics having improved light stability are obtained by incorporating diamines, such as piperazine, into the polyhydroxy compounds of relatively high molecular weight.

The use of aliphatic diisocyanates has, however, hitherto been very restricted both because it is often impossible to obtain from them polyurethanes having the required high-quality elastic properties and also because the lower reaction velocity of the aliphatic compounds is frequently, very disadvantageous.

Consequently, aromatic polyisocyanates are almost exclusively used in the art. Preferred aromatic polyisocyanates are the isomeric toluylene diisocyanates, naphthalene-1,5-diisocyanate and diphenylmethane - 4,4' - diisocyanate.

These diisocyanates have recently preferentially been used to prepare highly elastic fibres, foils, coatings and foam materials, since they sometimes impart excellent properties to polyurethanes.

Polyurethanes obtained from aromatic polyisocyanates, however, show a rapid and strong yellow to brown discolouration when exposed to sunlight or to artificial light, especially to sources radiating a high proportion of ultra-violet light. This discolouration is frequently accompanied by a decrease in the mechanical strength values of the polyurethanes.

Many auxiliary substances have been used to reduce the ageing of polyurethanes caused by light or oxygen and possibly the simul-

[P. 2]

taneous action of sunlight and artificial light, which ageing has a deleterious effect upon the mechanical properties of the polyurethanes. There have been employed, as auxiliary substances, antioxidants and/or ultra-violet absorbers, for example phenothiazine, phenyl-naphthylamine, dinaphthyl - *p* - phenylene diamine, 2 - mercapto - 2 - imidazoline and derivatives of  $\alpha, \alpha'$  - hydroxybenzophenone and 2,2' - dihydroxy - 3,3' di - *t* - butyl - 5,5' - dimethyldiphenylmethane. It has also been stated that certain hydrazones and esters of phosphorous acid reduce the degradation of polyurethanes by oxidation in light. Carbon black also has some antioxidant effect.

It is certainly possible in this way, to impart to polyurethanes some protection against degradation by oxygen, but the natural colours of the anti-oxidants and ultra-violet absorbers, or the discolourations they produce, are disturbing and their light-stabilising action is insufficient. To stabilise high quality colourless or brightly-pigmented materials, especially foam materials, foils, textile coatings and highly elastic fibres, it is necessary to employ stabilisers which have no natural colour and which are not discoloured by the action of light and/or oxygen.

The present invention provides synthetic plastics materials containing urethane groups and substantially free from isocyanate groups and stabilised against discolouration and oxidation by the presence of such a weight of hydrazide derivatives containing one or more -CO-NH-NH<sub>2</sub> and/or -CS-NH-NH<sub>2</sub> groups in the molecule that there are 10 to 2000 milligram equivalent of



groups per kilogram of polyurethane.

In this connection, the -CO-NH-NH<sub>2</sub> and -CS-NH-NH<sub>2</sub> groups behave as monofunctional groups.

The compounds employed in the present invention, hereinafter referred to for convenience as "hydrazide compounds" impart to synthetic plastics excellent stability against discolouration by sunlight and even by light containing a high proportion of ultra-violet.

It is now possible to produce from aromatic polyisocyanates synthetic plastics which have extraordinary light stability.

In the production of coatings, foils and especially highly elastic filaments, the strong adhesion shown by fresh surfaces of the moulded elements has hitherto been unpleasantly noticeable. It is true that these sticking properties could substantially be eliminated by treatment with talc, but the use of talc is very undesirable, especially for filaments used in the textile industry, since it results in considerable soiling and in a high

degree of wear of the corresponding machines and apparatus.

Non-tacky foils and filaments, which can be reeled and used without the aid of talc, are obtained by adding to the elastomeric substance a hydrazide derived from a fatty acid containing a relatively long carbon chain or from a dimerised fatty acid. Examples of suitable hydrazides are the hydrazides of palmitic, stearic and ricinoleic acid.

Suitable "hydrazide compounds" are hydrazides of carboxylic and other acids, such as acetic acid hydrazide, trimethyl-acetic acid hydrazide, acrylic acid hydrazide, undecanecarboxylic acid hydrazide, sorbic acid hydrazide, propionic acid hydrazide, benzoic acid hydrazide, picolinic acid hydrazide, stearic acid hydrazide, oleic acid hydrazide,  $\omega$ -hydroxybutyric acid hydrazide,  $\omega$ -hydroxycaproic acid hydrazide, tartaric acid dihydrazide,  $\alpha$ -isopropylsuccinic acid hydrazide,  $\omega$ -aminocaproic acid hydrazide,  $\omega$ -aminocapric acid hydrazide,  $\omega$ -aminoundecanoic acid hydrazide,  $\omega$ -aminododecanoic acid hydrazide, carbodihydrazide



oxalic acid bishydrazide, adipic acid bishydrazide,  $\beta$ -methyladipic acid bis-hydrazide, dodecane-dicarboxylic acid dihydrazide, terephthalic acid bis-hydrazide, isophthalic acid dihydrazide, benzene-tricarboxylic acid trishydrazide, terephthalic acid monomethyl ester hydrazide, terephthalic acid hydroxyethyl ester hydrazide and polyester hydrazides, such as those which are formed by reacting dicarboxylic acid/ethylene glycol polyester with small quantities of hydrazine to give "hydrazinolysis" of the ester bonds. Particularly suitable are semicarbazide, thiosemicarbazide, hexyl semicarbazide, 1,4-tetramethylene - bis - semicarbazide, 1,6-hexamethylene - bis - semicarbazide, 1,6-hexamethylene - bis - thiosemicarbazide and piperazine -  $\text{N}_2\text{N}'$  - dicarboxylic acid hydrazide. Other suitable compounds are bydrazine carboxylic acid and its esters, such as hydrazinecarboxylic acid *n* - octyl ester, ethyleneglycol - bis - carbazine ester, 1,4-butyleneglycol - bis - carbazine ester and compounds such as hydrazine-dicarboxylic acid dihydrazide and iminodicarboxylic acid dihydrazide.

For the stabilisation of fibres or foils which are subjected to washing processes, it is advisable, in order to produce permanent protection against the action of light, to use those hydrazide compounds which are sparingly soluble or insoluble in water. Examples of such compounds are the hydrazides of long chain fatty acids, bis-semicarbazides and hydrazide derivatives of aromatic dicarboxylic acids. It is, however, preferred to use

- hydrazide compounds of molecular weight from 800 to 5000, such as those which are obtained by reacting polyesters with enough hydrazine hydrate to effect partial hydrazinolysis of the ester bonds. These latter hydrazide compounds are highly compatible with polyurethane. There are also a number of other processes for obtaining such compounds of relatively high molecular weight which contain free  $-\text{CO} \cdot \text{NH} \cdot \text{NH}_2$  groups, for example the reaction of a dicarboxylic acid dihydrazide with a less than molar quantity of a bis-acid chloride or bis-chlorocarbonic acid ester of an aliphatic, aromatic or heterocyclic compound, or by reacting a dicarboxylic acid dihydrazide with a less than molar quantity of a polyisocyanate or polyisothiocyanate. The reaction product of, for example, 1 mol. of hexamethylene diisocyanate and 2 mols. of  $\omega$ -amino-caproic acid hydrazide may also be used.
- Aromatic sulphonic acid hydrazides, for example, 1,3-phenylene disulphonic acid dihydrazide, not only afford no protection against discolouration in sunlight, but lead, in fact, to a more rapid discolouration than is obtained without addition of a hydrazide compound.
- Other unsuitable compounds are the reaction products of the hydrazide compounds with isocyanates, for example the reaction product of 1 mol. of carbodihydrazide and 2 mols. of phenyl-isocyanate, the reaction product of 1 mol. of hexamethyl-bis-semicarbazide and 2 mols. of phenylisocyanate, the reaction product of phenylsemicarbazide and phenylisocyanate, the reaction product of butane-bis-carbazine ester and 2 mols. of phenylisocyanate and the reaction product of hydroxyethyl hydrazine and phenylisocyanate. These latter compounds are not light stabilisers, since it is the free  $-\text{CO} \cdot \text{NH} \cdot \text{NH}_2$  or  $-\text{CS} \cdot \text{NH} \cdot \text{NH}_2$  group that provides the stabilising action.
- The synthetic plastics containing urethane groups which may be stabilised by the present process may be prepared in known manner by polyaddition from polyhydroxy compounds of relatively high molecular weight, polyisocyanates and, if desired, chain extenders containing active hydrogen atoms, such as water, hydroxy compounds, amines, hydrazines and hydrazide compounds. Synthetic plastics produced by reacting chlorocarbonic acid esters of relatively high molecular weight and polyhydroxy compounds with, for example, aliphatic diamines or hydrazine may also be stabilised according to the present invention.
- Synthetic plastics containing urethane groups can be stabilised with the hydrazide compounds in any of the forms in which they exist, for example as elastic moulded elements, soft rollers, foam materials, foils, coatings and filaments. These synthetic plastics are usually obtained without alteration by known processes, generally from polyhydroxy compounds (for example polyesters, polyethers, polythioethers, polyacetals and polyisocyanates) and, if desired, chain extenders, irrespective of whether all the reactants are reacted simultaneously or whether the high molecular weight product is formed in stages. The incorporation of the hydrazide compounds takes place when the reaction between the isocyanate component and the polyhydroxy compound is substantially complete that is to say it takes place in practice in the prepared plastic, so that the hydrazide compounds which *per se* react with isocyanate groups are not eliminated and thus do not lose their activity.
- The hydrazide compounds acting as stabilisers can be incorporated into the synthetic plastics that contain urethane groups by various methods, which are determined by practical convenience.
- The simplest method is to add the hydrazide compounds in dissolved form to solutions of the polyurethane compositions. Suitable solvents are dimethyl formamide, dimethylacetamide and dimethylsulphoxide, if desired in admixture with other solvents or water.
- Insoluble hydrazides can be incorporated into the solutions in an extremely finely powdered form, if desired, together with pigments, but, generally, larger quantities are necessary than if the addition is made in solution.
- The hydrazide compounds can be incorporated on rollers into synthetic plastics which are not in solution, and perhaps into the elastomers. Application of the hydrazide compounds by, for example dipping or spraying, is also possible and is suitable for foam materials. By using the quantities of the hydrazide compounds according to the invention it is generally found that they are employed in an amount from 0.1 to 10% by weight, preferably from 0.5 to 3% by weight, based on the solid substance of the polyurethane composition.
- In addition to the hydrazide compounds, other agents which protect the polyurethanes against light and oxidation may concurrently be employed, it being necessary to use colourless or non-discolouring anti-oxidants to stabilise colourless polyurethanes. Examples of such antioxidants are esters of phosphorous acid, such as trinonyl phosphite and triphenyl phosphite, and hydroxy derivatives of benzophenone or diphenylmethane, which may be substituted by, for example, alkyl or alkoxy groups. Pigments and fillers such as titanium dioxide and silica gel may also be added to the polyurethanes.
- Polyurethane compositions which have been obtained using hydrazide compounds as chain extenders often show a discolouration, which is produced by traces of metal in combination with the residue of the hydrazide compounds. It has been found that by adding the stabil-

isers according to the invention, this discolouration can also be suppressed. For this purpose it is additionally possible for compounds of tin, antimony and beryllium to be incorporated into the polyurethane compositions.

In the following Examples (in which all parts and percentages are by weight), the improvement in the light stability is shown in most cases with foils which have been produced from solutions. These results are comparable to the effects which can be produced with filaments.

Because of the fundamentally different light stabilities of products derived from different isocyanates and chain extenders, the periods of the stabilisation against discolouration in light can differ. A substantial improvement in the light stability is, however, always produced by addition of the hydrazide compounds.

#### EXAMPLE 1

3500 g. of an ethyleneglycol/butyleneglycol (1:1)-adipic acid polyester (OH number 53.25; acid number 1.40) are dehydrated for 1 hour at 130° C and 12 mm. Hg.; 3 ml. of a 38% solution of sulphur dioxide in dioxane are then added and the resulting mixture is heated with 791 g. of diphenylmethane-4,4'-diisocyanate in 1839 g. of anhydrous chlorobenzene for 130 minutes in a boiling water bath while stirring in an atmosphere of nitrogen. After standing for 16 hours at room temperature, the NCO content is 1.85%.

5788 g. of the polyester isocyanate solution thus obtained are reacted at room temperature continuously and with vigorous stirring, with a solution of 114.7 g. of carbodihydrazide in 716 g. of water and 16581 g. of dimethylformamide. A solution of the polyurethane elastomer containing substantially no free hydrazide groups and having a viscosity of 37.5 poises/20°C and a solids content of 18%, is thus obtained.

This solution is pigmented with 5% of TiO<sub>2</sub> (based on the weight of solids content) by adding a titanium dioxide paste in dimethylformamide, and concentrating in a thin-film evaporator to a concentration of 23% and a solution viscosity of 516 poises/20°C. The limiting viscosity  $\eta_{\text{lim}} = \frac{\eta}{C}$  of the polymeric

substance is 1.05 with a concentration of 1 g./100 ml. of phosphoric acid trisdimethylamide after dissolving for 3 hours at 20°C.

100 g. samples of the pigmented polyurethane elastomer solution are mixed with the quantity of hydrazide compound indicated in the following Table (in percentage by weight, based on solid substance of the solution), dissolved in dimethylformamide or dimethylformamide/water, or as a suspension produced on a roll stand, and cast by means of a casting means into foils having a thickness of about 0.20 mm. after drying (45 minutes/70° C and 45 minutes/100° C).

Nature of the hydrazide compound	Concentration (%)	Colour of film after exposure in an ATLAS fadeometer for		
		10 hours	20 hours	50 hours
no hydrazide compound	—	slightly yellowish	yellowish to yellow	yellowish-brown
Carbodihydrazide	2	completely colourless	completely colourless	colourless
	1	„	„	„
	0.5	„	„	slightly yellowish
Adipic acid dihydrazide	2	colourless	colourless	slightly yellowish
$\epsilon$ -hydroxycaproic acid hydrazide	2	colourless	colourless	yellowish
$\epsilon$ -Aminocaproic acid hydrazide	2	colourless	colourless	yellowish
<i>m</i> -Xylylene-bis-semicarbazide	2	colourless	colourless	colourless
Piperazine-N,N <sup>1</sup> dicarboxylic acid dihydrazide	2	colourless	colourless	colourless
Isophthalic acid dihydrazide	2	colourless	colourless	yellowish
Terephthalic acid monobutyl ester hydrazide	2	colourless	slightly yellowish	yellowish
Reaction product of 200 g. of an ethylene-glycol/adipic acid polyester (molecular weight 2000) with 20 g. of hydrazine hydrate	3	colourless	slightly yellowish	yellowish
hydrazine-dicarboxylic acid dihydrazide	2	colourless	slightly yellowish	yellowish
Semicarbazide	2	colourless	yellowish	yellow
thiosemicarbazide	2	colourless	yellowish	yellow
Hexamethylene-bis-semicarbazide + palmitic acid hydrazide (1:5 mixture)	3	colourless	colourless	colourless
On the other hand, the following compounds show no stabilising action:				
1,3-Phenylene-disulphonic acid dihydrazide	2	brown	very brown	very dark brown
1,5-diphenylcarbodihydrazide	2	yellowish	yellowish-brown	brownish-yellow
reaction product of hydroxyethylhydrazine (1 mol) + phenylisocyanate (2 mol)	2	yellowish	yellowish-brown	brownish-yellow
reaction product of butanediol-bis-carbazine ester (1 mol) + phenylisocyanate (2 mol)	2	yellowish	yellowish-brown	brownish-yellow
2-mercapto-1,2-imidazoline	2	yellow	yellowish-brown	brownish yellow

## EXAMPLE 2

2000 g. of the pigmented solution employed in Example 1 and having a solution viscosity of 510 poises/20°C. are mixed while stirring with 3.45 g. of hexamethylene-bis-semicarbazide (0.75% based on solid content) and 11.5 g of palmitic acid hydrazide (2.5% based on solid content) dissolved in a little hot dimethylformamide.

The solution is spun, at a rate of 7.5 g./min., through a spinneret having 16 nozzles each of diameter 0.2 mm., into a spinning shaft having a length of 4.5 m. and which is heated to 210°C. The shaft is traversed by hot air (40 cubic metres hour; 250°C). The filaments are wound onto bobbins at the rate of 133 m/min.

The highly-elastic filaments have a non-tacky smooth surface and can be wound and rewound without using preparatory agents or talc. Filaments spun without addition of palmitic acid hydrazide show a very strong adhesion and produce on the bobbins masses of filaments which cannot be unwound. It is only by the use of talc, silica gel or other preparatory agents that filaments which can be unwound are obtained.

The filaments with addition of hydrazide compound show practically the same stability with respect to light and the effects of oxidation as the corresponding fcils produced as described in Example 1.

## EXAMPLE 3

50 g. of a polytetramethylene ether glycol (OH number 44) and 150 g. of a hexanediol/methylhexanediol - (1:1) - adipic acid polyester (OH number 60.1; acid number 1.23) are jointly dehydrated for 1 hour at 130°C/

12 mm. Hg. and mixed with 40 g. of distilled diphenylmethane-4,4'-diisocyanate, dissolved in 60 g. of benzene. The benzene is distilled off *in vacuo*, and the mixture is heated for 45 minutes in a boiling water bath while stirring under an atmosphere of nitrogen. After cooling, the isocyanate content of the melt is 2.12%. The melt is taken up in 230.5 g. of dimethylformamide at 35—40°C and the isocyanate content thereof is found by titration to be 0.96%.

This solution is reacted with a chain extender according to the procedures (a) to (c).

(a) 100 g. of the solution are diluted with 100 g. of anhydrous dimethylformamide and a solution of 1.03 g. of carbodihydrazide in 99 g. of dimethylformamide is added at a temperature of 65°C while stirring vigorously, a slightly yellowish solution having a viscosity of 212 poises/20°C. being formed within a few seconds.

(b) 200 g. of the solution are diluted with 200 g. of anhydrous dimethylformamide and reacted, while stirring vigorously, with a solution of 1.143 g. of hydrazine hydrate in 194 g. of dimethylformamide to form a greenish-yellowish solution having a viscosity of 307 poises/20°C.

(c) 100 g. of the solution diluted with 100 g. of dimethylformamide, are reacted with 715 mg. of 96% ethylene diamine in 97 g. of dimethylformamide.

Carbodihydrazide is added to the solutions of prepared polyurethane compositions obtained according to the procedures (a) to (c) and, after casting to form films the yellowing is determined in a Fadeometer:

Carbodihydrazide		0 hours	5 hours	10 hours	20 hours	50 hours
(a)	without	colourless	slightly yellowish	yellowish	yellow	yellowish-brown
	1%	colourless	colourless	colourless	colourless	yellowish
	2%	colourless	colourless	colourless	colourless	colourless
(b)	without	yellow	slightly yellowish	yellowish	yellow	yellowish brown
	1%	yellow	colourless	colourless	colourless	yellowish
	2%	yellowish	colourless	colourless	colourless	colourless
(c)	without	colourless	slightly yellowish	yellow	yellow	yellow
	1%	colourless	colourless	colourless	slightly yellowish	yellow
	2%	colourless	colourless	colourless	colourless	yellowish

## EXAMPLE 4

250 g. of polytetramethylene ether glycol (OH number 44) are dehydrated for 1 hour at 120°C/12 mm. Hg. and, after cooling, heated over a boiling water bath with a solution of 44.2 g. of diphenylmethane-4,4'-diisocyanate in 126 g. of chlorobenzene for 3 hours while stirring in an atmosphere of nitrogen. The isocyanate content of the solution is 1.755%.

410 g. of the solution are diluted at room temperature with 164 g. of anhydrous dimethylformamide to form a 50% solution: NCO content 1.25%. This solution is further processed according to the procedures (a) and (b).

(a) 100 g. of the 50% solution are diluted with 50 g. of dimethylformamide and a solution of 1.48 g. of carbodihydrazide in 100 g. of dimethylformamide is added while stirring

vigorously. A very tough and not entirely homogeneous solution is obtained, which becomes practically homogeneous after heating for 3 hours at 70°C. The resulting solution has a viscosity of 370 poises/20°C.

(b) 250 g. of the 50% solution are diluted with 300 g. of dimethylformamide and a solution of 1.87 g. of hydrazine hydrate in 75 g. of dimethylformamide is added while stirring. A viscous solution is obtained, which has a solution viscosity of 145 poises/20°C. after heating for 5 hours at 75°C.

200 mg. of carbodihydrazide (I) or hexamethylene-bis-semicarbazide (II) dissolved in 5 ml. of dimethylformamide, are added to 50 g. samples of each of the solutions (a) and (b) which have a solids content of 20%. The samples are cast to form foils having a thickness of about 0.20 mm. (final heating time 45 minutes/70°C and 45 minutes/100°C).

## Amount of Hydrazide Compound

## Light Exposure in the Fadeometer

		1	11	0 hours	10 hours	20 hours	50 hours
(a)	without	without	without	colourless	yellow	yellow	yellowish brown
	2%	without	without	colourless	colourless	colourless	yellow
	without	2%	2%	colourless	colourless	colourless	colourless
(b)	without	without	without	colourless	slightly yellowish	yellowish	pale yellow
	2%	without	without	colourless	colourless	colourless	colourless
	without	2%	2%	colourless	colourless	colourless	colourless

## EXAMPLE 5

This Example describes the stabilisation of a polyurethane polymer cross-linked to about 80% with carbodihydrazide and about 20% by water. The aromatic urea groups which are formed with the cross-linking with water show a strong brown colouring in sunlight and in the Fadeometer.

350 g. of an ethyleneglycol/butanediol-(1:1)-adipic acid polyester (OH number 53.25; acid number 1.40) are dehydrated for 1 hour at 130°/12 mm.Hg. and deactivated by introducing 7 bubbles of SO<sub>2</sub> per second at 75°C for 5 minutes and heated with a solution of 74.7 g. of 4,4'-diphenylmethane diisocyanate in 182 g. of chlorobenzene for 60 minutes at 95°C. After cooling and standing overnight, the solution has an isocyanate content of 1.61%.

500 g. of the solution obtained are thoroughly stirred at room temperature with a solution of 6.84 g. of carbodihydrazide in 70 g. of water and 800 g. of dimethylformamide. A highly viscous solution having a viscosity of 525 poises/20°C. is obtained. This solution quickly acquires a yellowish brown discolouration.

250 mg. of carbodihydrazide are added to 100 g. of the solution of the prepared, spinable polyurethane elastomer (1% based on the solid content). A brightening of the solution occurs. A film is obtained therefrom by spreading the solution and drying (45 min./70°C and 45 min./100°C). The resulting film is exposed to light in an ATLAS Fadeometer and compared with a similar film containing no additive:

	5	10	20	50 hours
without additive	deep yellow	yellow-brown	deep yellowish brown	deep brownish yellow
1% of carbodihydrazide	colourless	colourless	colourless	pale yellow

If the films are heated for 6 to 8 hours in boiling tap water, the film which does not contain an additive becomes discoloured, whereas the film containing the additive remains colourless.

#### EXAMPLE 6

100 g. of an ethyleneglycol-1,2-propyleneglycol - (80:20) - adipic acid polyester (molecular weight 2000) are quickly and thoroughly stirred at 100°C. with 1.50 g. of butane-1,4-diol and with 17 g. of molten 4,4'-diphenylmethane diisocyanate and cast to form sheets which are finally heated for 24 hours at 100°C.

50 g. of the material thus prepared are shredded and dissolved in 125 g. of dimethylformamide at 60°C over a period of 7 hours. In each case, 50 g. of the solution are stirred with 250 mg. (2%, based on solid substance) of carbodihydrazide or with 250 mg. of hexamethylene-bis-semicarbazide, dissolved in 7 ml. of dimethylformamide and cast into films having a thickness of about 0.2 mm. (drying time 45 min./70°C and 45 min./100°C).

On exposure to light in an ATLAS Fadeometer, the following results are obtained:

#### Exposure times in the Fadeometer

	0 hours	10 hours	20 hours	50 hours
Without additive	yellowish	brown	brown	very dark brown
2% carbodihydrazide	colourless	colourless	colourless	yellowish
2% hexamethylene-bis-semicarbazide	colourless	colourless	slightly yellowish	yellowish

#### EXAMPLE 7

A soft foam plastic (I) is prepared from an ethylene - glycol - adipic acid polyester, toluylene diisocyanate (65% of 2,4-isomer and 35% of 2,6-isomer) and water in the usual manner and a soft foam plastic (II) is obtained from polypropylene ether glycol,

toluylene diisocyanate and water. Both foam plastics are saturated for 2 minutes in an 18% aqueous solution of carbodihydrazide, wrung out on rollers and dried at room temperature, giving products comprising 330 milligram equivalents of carbodihydrazide per kilogram of polyurethane.

#### Exposure in Fadeometer

	10	20	50 hours
(I) without saturation	slightly brown	brown	deep brown
with saturation	colourless	pale yellowish	pale yellow
(II) without saturation	yellow	deep yellow, crumbling on the surface	deep yellow, 75% destroyed
with saturation	colourless	colourless, without degradation phenomena	yellowish, without destruction



## EXAMPLE 8

The procedures (I)—(IV) are for the purpose of comparison with prior art. The procedures V and VI correspond to the invention.

- 5 600 g of a polyester prepared from adipic acid, hexane diol and 2,2-dimethylpropane diol (molar proportion of glycol 65:35: OH number 60.4: acid number 1.4) are heated
- 10 to 100°C for 125 minutes with 135.4 g of 4,4'-dimethyl methane diisocyanate and 184.6 g of anhydrous dioxane. After cooling the NCO content is 1.79. The solution is passed within 5 minutes while stirring vigorously
- 15 into a 70°C solution of 18.92 g carbodihydrazide in 1968 g dimethyl formamide. The solution is then pigmented with 56.5 g of a 33% paste of titanium dioxide in dimethyl formamide. After cooling the solution has a viscosity of 204 Poise/20°C. After adding 0.745
- 20 g hexamethylene diisocyanate by stirring the viscosity increase to 695 Poise/20°C. The following additives are added in the quantities given (in % by weight, calculated on the solids content of the solution) to the pigmented spinning solution.
- 25 (I) no additive  
(II) 5% poly - (N,N - dimethylaminoethyl-methacrylate).
- 30 dissolved in warm dimethylformamide. The solution remains colourless.  
(III) 2% polyethylene imine, dissolved in aqueous dimethyl formamide.
- 35 The solution is coloured yellow-orange after few hours. Further the originally freely-flowing solution becomes an inhomogeneous pasty mass which can no longer, or only with difficulty be moulded.
- 40 (IV) 2% hexamethylene diamine, dissolved in a small quantity of dimethyl formamide. The solution is coloured yellow-orange withing a short time. The viscosity decreases quickly.
- 45 (V) 2% carbodihydrazide, dissolved in dimethyl formamide at 70°C. The solution remain colourless.
- 50 (VI) 2% hexamethylene - bis - semicarbazide, dissolved in dimethyl formamide at 70°C. The solution remains colourless.

The solutions are cast onto glass plates. After evaporating the solvent (45 minutes at 70°C

and 45 minutes at 100°C) highly elastic films 1.5 mm thick are obtained. The films I, II, V and VI are colourless, while the films III and IV have a remarkably yellow colouration right from the start. In an Atlas fadeometer the films are treated under equal conditions for 10, 20 and 50 hours. Then also the films I and II show a strong discolouration.

## WHAT WE CLAIM IS:—

1. Synthetic plastics materials containing urethane groups and substantially free from isocyanate groups which are stabilised against discolouration and oxidation by the presence of such a weight of hydrazide derivatives containing one or more  $\text{—CO—NH—NH}_2$  and/or  $\text{—CS—NH—NH}_2$  groups in the molecule that there are 10 to 2000 milligram equivalent of

$\text{—CO—NH—NH}_2$  and/or  $\text{—CS—NH—NH}_2$

groups per kilogram of polyurethane.

2. Materials as claimed in claim 1 wherein the hydrazide derivatives are carboxylic acid hydrazides.

3. Materials as claimed in claim 1 wherein the hydrazide derivatives are polyester hydrazides.

4. Materials as claimed in claim 1 wherein the hydrazide derivatives are semicarbazides or thiosemicarbazides.

5. Materials as claimed in claim 1 wherein the hydrazide derivatives are insoluble or sparingly soluble in water.

6. Materials as claimed in claim 1 wherein the hydrazide derivatives have been obtained by reacting polyesters with hydrazine.

7. Materials as claimed in claim 1 wherein the hydrazide derivatives have been obtained by reacting a dicarboxylic acid dihydrazide with a less than molar quantity of a bis-acid or of a bis-chlorocarbonic acid ester of an aliphatic, aromatic or heterocyclic compound.

8. Materials as claimed in claim 1 wherein the hydrazide derivatives have been obtained by reacting a dicarboxylic acid dihydrazide with a less than molar quantity of a polyisocyanate or polyisothiocyanate.

9. Materials as claimed in claim 1 substantially as described with reference to any of the Examples.

ELKINGTON AND FIFE,

Chartered Patent Agents,

Bank Chambers,

329, High Holborn, London, W.C.1.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1966. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.